

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C10G 2/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/27181</b> <b>(43) International Publication Date:</b> 25 June 1998 (25.06.98)
<b>(21) International Application Number:</b> PCT/US97/23191 <b>(22) International Filing Date:</b> 15 December 1997 (15.12.97) <b>(30) Priority Data:</b> 60/033,375 16 December 1996 (16.12.96) US <b>(71) Applicant (for all designated States except US):</b> RENTECH, INC. [US/US]; Suite 720, 1331 17th Street, Denver, CO 80202 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> BENHAM, Charles, B. [US/US]; 7234 S. Jellison Court, Littleton, CO 80123 (US). BOHN, Mark, S. [US/US]; 1614 Tamarac Drive, Golden, CO 80401 (US). YAKOBSON, Dennis, L. [US/US]; 12544 W. 87th Avenue, Arvada, CO 80005 (US). <b>(74) Agents:</b> BERKSTRESSER, Jerry et al.; Shoemaker and Mattare, Ltd., Suite 1203, 2001 Jefferson Davis Highway, Arlington, VA 22202 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> CATALYST/WAX SEPARATION DEVICE FOR SLURRY FISCHER-TROPSCH REACTOR		
<b>(57) Abstract</b> <p>Catalyst particles are separated from the wax in a Fisher-Tropsch reactor by feeding a portion of the reactor slurry to a dynamic settler which does not require any pump. As the slurry flows down a pipe in the center of the settler, the slurry flows into the surrounding annular region at the bottom of the settler. The heavier catalyst particles settle down and are removed as the slurry at the bottom of the settler is recycled back to the reactor. The wax rises up in the annular section and this clarified wax is removed by a wax outlet pipe. In an embodiment with an expanded diameter section above the Fisher-Tropsch reactor an additional dynamic settler can be placed inside this section. The Fischer-Tropsch catalyst can be regenerated by purging the catalyst with an inert gas for a period of time and by treating the catalyst with naphtha.</p> <p><i>heavier catalyst particles centrifugation of catalyst separating.</i></p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

CATALYST/WAX SEPARATION DEVICE FOR SLURRY  
FISCHER-TROPSCH REACTOR

Background of the Invention

1. Field of the Invention

5        This invention relates to the application of Fischer-Tropsch chemistry to conversion of synthesis gas (hydrogen and carbon monoxide) to liquid hydrocarbons. In particular it relates to a Fischer-Tropsch reactor wherein the gases react in a slurry of catalyst powder suspended in molten  
10       wax. Such a slurry reactor has associated with it special problems in removing wax products from the reactor without removing fine catalyst particles as well.

2. Description of the Previously Published Art

15       In a slurry reactor in which a mixture of hydrogen and carbon monoxide are reacted on a powdered catalyst to form liquid hydrocarbons and waxes (Fischer-Tropsch reaction), the slurry is maintained at a constant level by continuously or intermittently removing wax from the  
20       reactor. The problem with wax removal is that catalyst in the wax must be separated from the slurry and returned to the reactor to maintain a constant inventory of catalyst in the reactor. Also, in order to keep the catalyst losses within the required replacement rate due to deactivation,  
25       the clarified wax removed from the system must not contain more than about 0.25% catalyst by weight. Several means have been proposed for separating the catalyst from the wax, e.g., centrifuges, cross-flow sintered metal filters, magnetic separators, etc.

30       The separation task is the most challenging when the catalyst produces free carbon and/or when particles break down during operation to produce "fines" which are sub-micron in size. In this case, it has been found that the

- 2 -

small particles clog sintered metal filters to the point that back washing is ineffective. Also, centrifuges have been found unsuccessful in reducing the catalyst concentration below about 1 % by weight in the clarified wax being removed.

Several methods have been described for separating catalyst particles from Fischer-Tropsch wax. A comprehensive report on the subject in entitled "Status Review of Fischer-Tropsch Slurry Reactor/Catalyst Wax Separation Techniques" prepared for the U.S. Department of Energy, Pittsburgh Energy Technology center by P. Z. Zhou, Burns and Roe Services Corporation, February, 1991. In this document are described filters, magnetic separators and settling devices, most of which were not successful or were not deemed commercially viable.

### 3. Objects of the Invention

It is an object of the invention is to provide an improved process for separating wax and catalyst whereby a relatively clean wax can be removed from the slurry reactor and the catalyst can be returned to the reactor without being subjected to attrition from a mechanical pump.

It is a further object of this invention to provide a catalyst particle separation device where the catalyst slurry obtains momentum as a jet as it issues from the feed conduit into the settler and where this momentum carries the catalyst particles in the settler in a direction opposite to that of the wax being removed from the settler.

It is a further object of this invention to provide a settler design where the combination of high upward velocities and a wire mesh filter within the settler

- 3 -

enables the size and number of dynamic settlers to be reduced dramatically.

It is a further object of this invention to provide an expanded diameter section in a Fischer-Tropsch reactor which serves as a catalyst disengaging section so that the number of settlers required to remove wax of a specific clarity is reduced.

It is a further object of this invention to regenerate and to increase the activity of a Fischer-Tropsch catalyst as well as to restore and maintain the selectivity of the catalyst by purging the catalyst with an inert gas for a period of time.

It is a further object of this invention to maintain the activity and selectivity of the catalyst more nearly constant over time in a slurry Fischer-Tropsch reactor by washing the catalyst with naphtha.

These and further objects of the invention will become apparent as the description of the invention proceeds.

#### Summary of the Invention

A dynamic settler apparatus is used for catalyst and wax separation from a slurry in a Fischer-Tropsch (F-T) reactor. A portion of the reaction slurry containing wax and the catalyst particles is removed for catalyst separation by feeding the slurry to at least one dynamic settler. The settler has a sealed vertical chamber into which a vertical feed conduit extends downwardly into the settler chamber for a substantial length so as to form an annular region between the inner walls of the chamber and the feed conduit. At the lower portion of the settler chamber there is a slurry removal outlet for removal of the

- 4 -

slurry to be returned back to the F-T reactor. As the slurry flows into the annular region at the bottom of the settler the heavier catalyst particles are carried down and are removed as the slurry at the bottom of the settler is recycled back to the reactor. The wax rises up in the annular section and this clarified wax is removed by a wax outlet pipe at the top. The outlet pipe can optionally have a filter to further purify the wax.

In another embodiment the upper portion of the F-T reactor can have an expanded section for removal of the catalyst slurry since the slurry in this region has a lower catalyst concentration. This expanded diameter section above the reaction zone can also have a further internal dynamic settler positioned inside and the wax removed in the upper portion of the annular zone can be sent to an external dynamic settler for improved results.

The Fischer-Tropsch catalyst can be regenerated and have its activity increased as well as restoring and maintaining the selectivity of the catalyst by purging the catalyst with an inert gas for a period of time.

The activity and selectivity of an iron-based or cobalt-based catalyst for a slurry phase F-T reactor can be maintained by treating the catalyst slurry with naphtha.

#### Brief Description of the Drawing

Fig. 1 illustrates the slurry reactor and the adjacent dynamic settler for separating the catalyst and wax.

- 5 -

Fig. 2 illustrates the system of Fig. 1 with an additional wire mesh filter in the settler.

Fig. 3 illustrates a slurry reactor with an expanded diameter section from which the slurry is removed and it also illustrates the use of more than one dynamic settler.

Fig. 4 illustrates a slurry reactor with an expanded diameter section having an internal dynamic settler in that section as well as an external dynamic settler.

#### Description of the Preferred Embodiments

10 If the catalyst particles to be separated are sufficiently large and do not attrit during operation or to the grinding action of a mechanical pump, then conventional filters, either of the sintered metal cross-flow type (manufactured by Mott Metallurgical) or of the wire mash  
15 type (manufactured by Pall Filter Corp.) can be used.

However, when there are small, i.e. submicron, catalyst particles present, filtration becomes a challenge. The challenge becomes even greater when the catalyst contains and/or is mixed with carbon which can permanently  
20 plug a sintered metal filter due to the tortuous path of the pores. In this case, it is desirable to use a wire mesh filter which does not have long tortuous pores to plug. With a wire mesh filter, it has been found that the total concentration of catalyst as well as the percentage of  
25 "fines" on the filter is important in establishing the required time intervals between back-washings for a given mesh size of the filter. Thus, if a mesh filter is placed within the reactor where the catalyst concentration is greater than say 4% by weight, the filter will require  
30 back-washing too frequently. By using upstream of the mesh filter the dynamic settler to be discussed below, the

- 6 -

catalyst concentration on the filter can be reduced to below 4% thereby enabling the filter to operate efficiently with longer periods of time between back-washings.

5 The dynamic settler is a device which accomplishes the desired catalyst/wax separation and simultaneously returns the removed catalyst to the reactor. An important feature of the device is that it is passive, i.e., it requires no pumps for moving the slurry through the system. Referring to Figure 1, the three-phase mixture in slurry reactor 1 (sometimes referred to as a bubble column reactor) flows into overflow pipe 2 and thence to vertical disengaging pipe 3. The gas bubbles rise in the gas disengaging pipe 3 and flow into reactor outlet pipe 4. The liquid medium and solid catalyst particles flow downwards in the disengaging pipe 3 and enter pipe 5 which lies on the centerline of the cylindrical dynamic settler 6. Pipe 5 extends about 80% of the length of settler 6. The slurry exits pipe 5 as a free jet, flows into the exit opening of settler 6 and returns to the reactor through pipe 7. The annular region 8 surrounding pipe 5 contains wax which is essentially free from catalyst particles since the particles must undergo a 180° change in direction in order to flow upwards in the annular region. A valve 9 located at the top of settler 6 is used to control the rate of wax removal from the settler. Flow through the settler is maintained by natural circulation created by the difference in hydrostatic head between the gas-free slurry in settler 6 and the bubbly flow in reactor 1.

30 The efficacy of the device in removing catalyst particles from the slurry is due in part to the momentum of the jet issuing from pipe 5. This momentum carries the particles into pipe 7 in a direction opposite to that of the wax being removed from the device. Therefore, not only is gravity causing the particles to move downward, but also the momentum of the jet. Once the particles have been



- 7 -

separated from the jet, the clarity of the wax being removed is determined by the upward velocity of the wax in the annular region 8, i.e., a lower velocity entrains fewer particles than a higher velocity due to the lower drag force on the particles. Therefore, for a specified flow rate of wax to be removed, a diameter of settler 6 can be selected to give a sufficiently low upward velocity for a desired clarity of wax. The other components of the apparatus will be sized so as to produce the described functional result.

Table 1 is a tabulation of test data obtained using dynamic settlers mounted on a small slurry Fischer-Tropsch reactor using an iron-based catalyst which is known to break down into submicron size particles under reaction conditions. Table 1 includes some test data at high upward velocities using water and unreacted catalyst. The data shows the effect of upward velocity on the clarity of liquid removed from the separation device.

- 8 -

Table 1.

## Liquid/Catalyst Separation Test Data

Test	Settler Dia. (Cm)	Velocity (Cm/h)	% Catalyst
Wax/Cat	10.2	1.1	0.04
Wax/Cat	10.2	1.6	0.07
Wax/Cat	10.2	5.9	0.16
Hot Water/Cat	5.1	37.4	1.98
Hot Water/Cat	5.1	78.2	3.45
Cold Water/Cat	5.1	129.9	4.75
Cold Water/Cat	5.1	65.3	3.69
Cold Water/Cat	10.2	40.0	4.33
Cold Water/Cat	10.2	120.0	6.54
Cold Water/Cat	10.2	40.0	5.00
Cold Water/Cat	10.2	40.0	4.81

It can be observed in Table 1 that the catalyst content of the clarified liquid is rather high at high upward velocities in the settler. In order to remove the remaining catalyst in the clarified wax, a clay filter or a mesh filter 10 will be required. However, if a clay filter is used, the catalyst cannot be recovered and returned to the reactor. Thus, in order to keep the catalyst losses to an acceptably low level, the upward velocity in the settlers must be kept below about 6 cm/h. This low upward velocity requirement translates into a requirement for a very large number of settlers arranged in parallel to accommodate the wax production in a commercial reactor.

A serendipitous solution to the aforementioned dilemma was found by employing a wire mesh filter 11 (shown in Figure 2) within the annular region of the dynamic settler. Such a wire mesh filter is marketed by Pall Corporation

- 9 -

under the trade name Rigimesh. The wire mesh filter does not have tortuous paths of fine pores in which submicron particles can become lodged as does a sintered metal filter. However, the very small particles which are found  
5 in the annular region of the dynamic settler do not build up a filter cake on the wire mesh filter readily unless the concentration of particles is above about 2% by weight. If the concentration of catalyst is high, e.g., 10%, then the frequency of back-washing the filter will be too high. The  
10 high upward velocities in the settler which give excessively high catalyst losses without a filter, are ideal for use with a wire mesh filter. Therefore, this combination of high upward velocities and a wire mesh filter within the settler enables the size and number of  
15 dynamic settlers to be reduced dramatically.

If the catalyst particles do not break down to form submicron particles, e.g., a catalyst deposited on alumina or other refractory support, and free carbon is not produced in the reaction, a sintered metal filter can be  
20 mounted in the annular space inside the separation device in place of the wire mesh filter. In this case, a high filtration rate can be achieved due to the low catalyst concentration in the vicinity of the filter.

It is not necessary to place the filters inside the  
25 dynamic settlers. It may be found advantageous to combine the flows of clarified wax from several settlers before filtering in a separate filter. In this case, pairs of filters can be arranged in parallel for isolation and maintenance of one of the filters while the other filter  
30 remains in operation.

One other arrangement in lieu of external dynamic settlers is an array of internal settlers located in a region within the Fischer-Tropsch reactor above the cooling tubes or intermingled with the cooling tubes. This

- 10 -

arrangement has the advantage of not requiring heat tracing of the settlers.

In addition to the dynamic settler feature, the following additional features can be employed to reduce the number of settlers and to improve the performance of the overall system.

When large amounts of wax are produced in a slurry Fischer-Tropsch (F-T) reactor operating in a high-wax production mode, then a preferred embodiment is to remove the slurry from the reactor in an expanded diameter section above the reaction zone in the catalyst disengaging section. The slurry which is removed in this disengaging zone will have a lower concentration of catalyst and gas bubbles than the slurry which is removed from the smaller diameter reacting zone. For the same amount of catalyst in the expanded section as in the smaller diameter reacting zone, the concentration of catalyst particles is inversely proportional to the square of the diameter; therefore, an increase in diameter of 40% will reduce the concentration by 50%. The concentration of bubbles is reduced in the expanded section as well. Preferably the increase in diameter is at least about 20% with a more preferred increase being at least about 40%.

Fig. 3 illustrates a reactor 20 where a three-phase mixture of wax, catalyst and gas bubbles leaving the expanded diameter section 22 through slurry outlet pipe 24 and flowing into a gas disengaging pipe 26 where the bubbles flow upward into the gas space at the top of the expanded section 22. The degassed slurry flows downward into the settler 28 and through the slurry return pipe 30 to the slurry bubble column reactor 20 under natural convection due to the higher density of the degassed slurry over that of the bubble-laden slurry in the reactor. Clarified wax is removed from the settler through wax

- 11 -

outlet pipe 32. A second settler 34 with the same structure is shown on the other side of the reactor.

5 A concentric cylindrical baffle 36 extends from the top of the expanded section above the foam layer 38 (which occurs at the top of the slurry bed due to bubbles  
10 broaching the surface of the slurry) down below the outlet ports to the settlers. This baffle prevents catalyst particles from flowing downward along the wall into the outlet pipes to the settlers due to recirculation currents  
15 caused by upward flow of slurry along the centerline as shown in Fig. 3. The baffle is most effective when positioned close to the expanded section wall, i.e. approximately 6 inches or less. Configurations other than a cylindrical baffle can be employed, such as individual  
baffles for each settler port provided that flow of slurry from the top or sides into the ports is prevented. The top of the expanded section has the reactor outlet pipe 40 to remove the gases.

20 A heat exchanger 42 shown in Fig. 3 with one cooling tube for clarity to remove the exothermic heat generated in the smaller diameter reaction zone is not required in the expanded section since the concentration of reactants and catalyst are too low for a substantial exothermic reaction to take place. However, the heat exchanger can be extended  
25 into the expanded section or a separate heat exchanger can be placed in this section and still be within the scope of this invention.

30 By using this expanded diameter embodiment in the catalyst disengaging section, the number of settlers required to remove the wax of a specific clarity is reduced.

- 12 -

A further embodiment illustrated in Fig. 4 uses an internal settler in the upper expanded section in combination with an external settler for housing the wire mesh filter so that the catalyst and wax from the filter can be returned to the reactor using natural circulation without a pump.

In Fig. 4 the column reactor has a cooling heat exchanger 52 with one tube shown for clarity and an upper expanded section 54. In this expanded section is an internal settler 56 with the structure previously described. The wax concentrated slurry leaving the settler flows through slurry outlet pipe 58 to an external settler 60. In the top of the external settler is the wire mesh filter 62 as in the structure shown in Fig. 2 with filter 11. The clean wax leaves via the clean wax outlet pipe 64 and the wax and catalyst slurry returns to the reactor via slurry return line 66. In the expanded upper section the foam layer is shown as 68 and the gases leave via reactor outlet pipe 70.

A further embodiment of the invention which regenerates and increases the activity of the catalyst as well as restoring and maintaining the selectivity of the catalyst is to purge the reactor with an inert gas for a period of time. After the catalyst has been under operation for a few weeks, there is generally a reduction in activity and a shift in selectivity to products, i.e. less wax production. This purging restores some of the activity and selectivity of the catalyst. Examples of inert gases which can be used are nitrogen, carbon dioxide, methane, or even hydrogen that may be readily available at the plant site.

To be most effective, the purging should be carried out at operating temperature and atmospheric pressure in order to maximize the difference between the partial pressure of the heavy waxes and other products on the

- 13 -

catalyst surface and the partial pressure of these species in the inert gas phase. In some cases it may be preferable to treat a slipstream of slurry on a continuous basis rather than purging the entire reactor contents in situ. If  
5 a slipstream is to be treated, an effective approach would be to use supercritical CO<sub>2</sub>, i.e. carbon dioxide under supercritical conditions (> 31°C and > 1073 psia).

A further embodiment which aids in maintaining the activity and selectivity of the catalyst more nearly  
10 constant over time in a slurry F-T reactor is to wash the catalyst with naphtha.

It was discovered during a test in which F-T naphtha which had been caustic washed was recycled back into a slurry F-T reactor that the activity of the catalyst was  
15 more nearly constant with time than in a comparable test without naphtha injection. We believe that neutralization of F-T naphtha which has been produced by using an iron-based F-T catalyst is essential since tests have shown that the naphtha fraction produced by using an iron-based F-T  
20 catalyst contains a large amount of oxygenates including acids such as acetic acid which could be detrimental to the catalyst in high concentrations. Commercially available naphtha or naphtha produced using a cobalt-based F-T catalyst can be used without neutralization.

25 The catalyst can be treated with naphtha in either of two embodiments. In one, the naphtha is injected directly into the F-T reactor under operating conditions. When using an iron-based F-T catalyst, the hydrocarbon product contains a high percentage of olefins which can readsorb on  
30 the catalyst surface and continue growing into longer-chain hydrocarbons if injected back into the reactor slurry. Therefore, if the naphtha has less value than diesel fuel, it may be desirable to recycle some of the naphtha back

- 14 -

into the reactor to reduce the amount of naphtha and increase the amount of diesel fraction produced.

5 In the second embodiment, a slipstream of slurry is treated with naphtha under non-reacting conditions, e. g. at a lower pressure and higher temperature without synthesis gas. Under this second embodiment, conditions for naphtha treatment can be selected which are the most effective for catalyst regeneration.

10 It is understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of this invention.



- 15 -

WHAT IS CLAIMED IS:

1. A dynamic settler apparatus for catalyst and wax separation in a slurry Fischer-Tropsch reactor comprising:
  - a) a slurry Fischer-Tropsch reactor having a gas outlet means;
  - b) removal means to remove from the reactor a portion of the reaction slurry containing wax and catalyst particles and to flow the slurry downwardly to a vertical feed conduit;
  - c) at least one dynamic settler comprising
    - a) a sealed vertical chamber with said vertical feed conduit extending downwardly into the chamber a substantial length so as to form an annular region between the inner walls of the chamber and the feed conduit;
    - b) a slurry removal outlet at the lower portion of the chamber for removal of the slurry; and
    - c) a wax outlet pipe extending from the top of the annular region to remove the clarified wax which flows up in the annular region; and
    - d) a slurry return pipe between the slurry removal outlet and the reactor.
2. A dynamic settler apparatus according to Claim 1, wherein the dynamic settler is cylindrical.

- 16 -

3. A dynamic settler apparatus according to Claim 1, wherein the vertical feed conduit is in fluid connection to the gas outlet means overhead so as to permit the gas bubbles in the slurry to disengage and flow upwardly to the gas outlet means.
4. A dynamic settler apparatus according to Claim 1, further comprising a flow control means on the wax outlet pipe to control the rate of wax removal from the dynamic settler.
5. A dynamic settler apparatus according to Claim 4, wherein the flow control means is a valve.
6. A dynamic settler apparatus according to Claim 1, wherein the wax outlet pipe further comprises a filter means to remove any remaining catalyst particles in the clarified wax.
7. A dynamic settler apparatus according to Claim 6, wherein there are a plurality of dynamic settlers and a common filter means to clarify the wax.
8. A dynamic settler apparatus according to Claim 1, further comprising a filter for catalyst particles mounted in the annular space inside the dynamic settler to filter the wax before it leaves the settler.
9. A dynamic settler apparatus according to Claim 8, wherein the filter is a wire mesh filter.
10. A dynamic settler apparatus according to Claim 8, wherein the filter is a sintered metal filter.

- 17 -

11. A dynamic settler apparatus according to Claim 1, wherein the removal means to remove from the reactor a portion of the reaction slurry containing wax and catalyst particles comprises a further dynamic settler positioned inside the reactor.
12. A dynamic settler apparatus according to Claim 1, further comprising an expanded diameter reaction section above the reaction zone and wherein the removal means comprises at least one settler port to remove the slurry to be treated from the expanded diameter reaction section and to flow to an outlet pipe connected to the vertical feed conduit.
13. A dynamic settler apparatus according to Claim 1, wherein the diameter of the expanded diameter reaction section is at least about 20% greater than the diameter of the reaction zone.
14. A dynamic settler apparatus according to Claim 13, wherein the diameter of the expanded diameter reaction section is at least about 40% greater than the diameter of the reaction zone.
15. A dynamic settler apparatus according to Claim 12, further comprising a baffle in the expanded diameter reaction section above the reaction zone, said baffle being spaced from the settler port, whereby the catalyst particles are prevented from flowing downward along the wall into the outlet pipes to the settlers due to recirculation currents caused by upward flow of slurry along the centerline.
16. A dynamic settler apparatus according to Claim 15, wherein the baffles are individual baffles for each settler port, said baffle being positioned to prevent the flow of slurry from the top or sides into the ports.

- 18 -

17. A dynamic settler apparatus according to Claim 15, wherein the baffle is a concentric cylindrical baffle.
18. A dynamic settler apparatus according to Claim 17, wherein the concentric cylindrical baffle extends from the top of the expanded section above any foam layer which is formed on top of the slurry bed due to bubbles breaching the surface of the slurry, to down below the removal means which are connected to one or more settlers.
19. A dynamic settler apparatus according to Claim 17, wherein the concentric cylindrical baffle is spaced close to the expanded section wall and preferably about 6 inches from the wall.
20. A dynamic settler apparatus according to Claim 1, further comprising an expanded diameter reaction section above the reaction zone having a further internal dynamic settler positioned inside this section where the vertical feed conduit for the settler extends into the slurry in the expanded diameter reaction section above the dynamic settler.
21. A dynamic settler apparatus according to Claim 20, wherein the wax removal pipe from the internal dynamic settler transports the wax to at least one external dynamic settler.
22. A dynamic settler apparatus according to Claim 21, further comprising a filter for catalyst particles mounted in the annular space inside the external dynamic settler to filter the wax before it leaves the settler.
23. A dynamic settler apparatus according to Claim 22, wherein the filter is a wire mesh filter.

24. A dynamic settler apparatus according to Claim 22, wherein the filter is a sintered metal filter.
25. An apparatus according to Claim 1, further comprising gas purge means to purge the catalyst with inert gas to regenerate the catalyst.
26. An apparatus according to Claim 25, wherein the gas purge means supplies the inert gas into the reactor.
27. An apparatus according to Claim 26, wherein the inert gas is nitrogen, carbon dioxide, methane or hydrogen.
28. An apparatus according to Claim 25, further comprising a slipstream from the reactor and wherein the gas purge means supplies the inert gas into said slipstream.
29. An apparatus according to Claim 28, wherein the gas purge means supplies the inert gas into the slipstream from the reactor on a continuous basis.
30. An apparatus according to Claim 28, wherein the inert gas is nitrogen, carbon dioxide, methane, hydrogen or supercritical carbon dioxide.
31. A method for separating catalyst particles from wax in a reaction slurry in a Fischer-Tropsch reactor comprising:
  - a) removing a portion of the reaction slurry containing the wax and catalyst particles from the reactor for separation in a dynamic settler;
  - b) feeding the removed reaction slurry into a vertical feed conduit extending downwardly into a sealed vertical dynamic settler chamber a substantial length so as to form an annular region between the inner walls of the chamber and the feed conduit,

whereby as the slurry flows into the annular region at the bottom of the settler the heavier catalyst particles settle down and are removed as the slurry at the bottom of the settler is recycled back to the reactor while the wax rises up in the annular section and this clarified wax is removed by a wax outlet pipe; and

c) optionally further filtering the clarified wax in the wax outlet pipe.

32. A method for maintaining the activity and selectivity of an iron-based or cobalt-based catalyst for a slurry phase F-T reactor comprising treating the catalyst with naphtha.
33. A method according to Claim 32, wherein the naphtha is commercially available naphtha, naphtha produced using a cobalt-based F-T catalyst, or naphtha produced using a iron-based F-T catalyst which has been neutralized.
34. A method according to Claim 32, wherein the naphtha is injected directly into the F-T reactor under operating conditions to also produce longer-chain hydrocarbons.
35. A method according to Claim 32, wherein the naphtha is added to a slipstream of slurry under non-reacting conditions.
36. A method according to Claim 35, wherein the naphtha is added to a slipstream of slurry at a lower pressure, at a higher temperature, and without the presence of synthesis gas.
37. A method for maintaining the activity and selectivity of an iron-based or cobalt-based catalyst or a slurry phase F-T reactor comprising treating the catalyst with an inert gas to regenerate the catalyst.

- 21 -

38. A method according to Claim 37, wherein the inert gas is supplied into the reactor.
39. A method according to Claim 38, wherein the inert gas is nitrogen, carbon dioxide, methane or hydrogen.
40. A method according to Claim 37, wherein a slipstream is taken from the reactor and the inert gas is supplied to said slipstream.
41. A method according to Claim 40, wherein the inert gas is supplied into the slipstream on a continuous basis.
42. A method according to Claim 40, wherein the inert gas is nitrogen, carbon dioxide, methane, hydrogen or supercritical carbon dioxide.

1/4

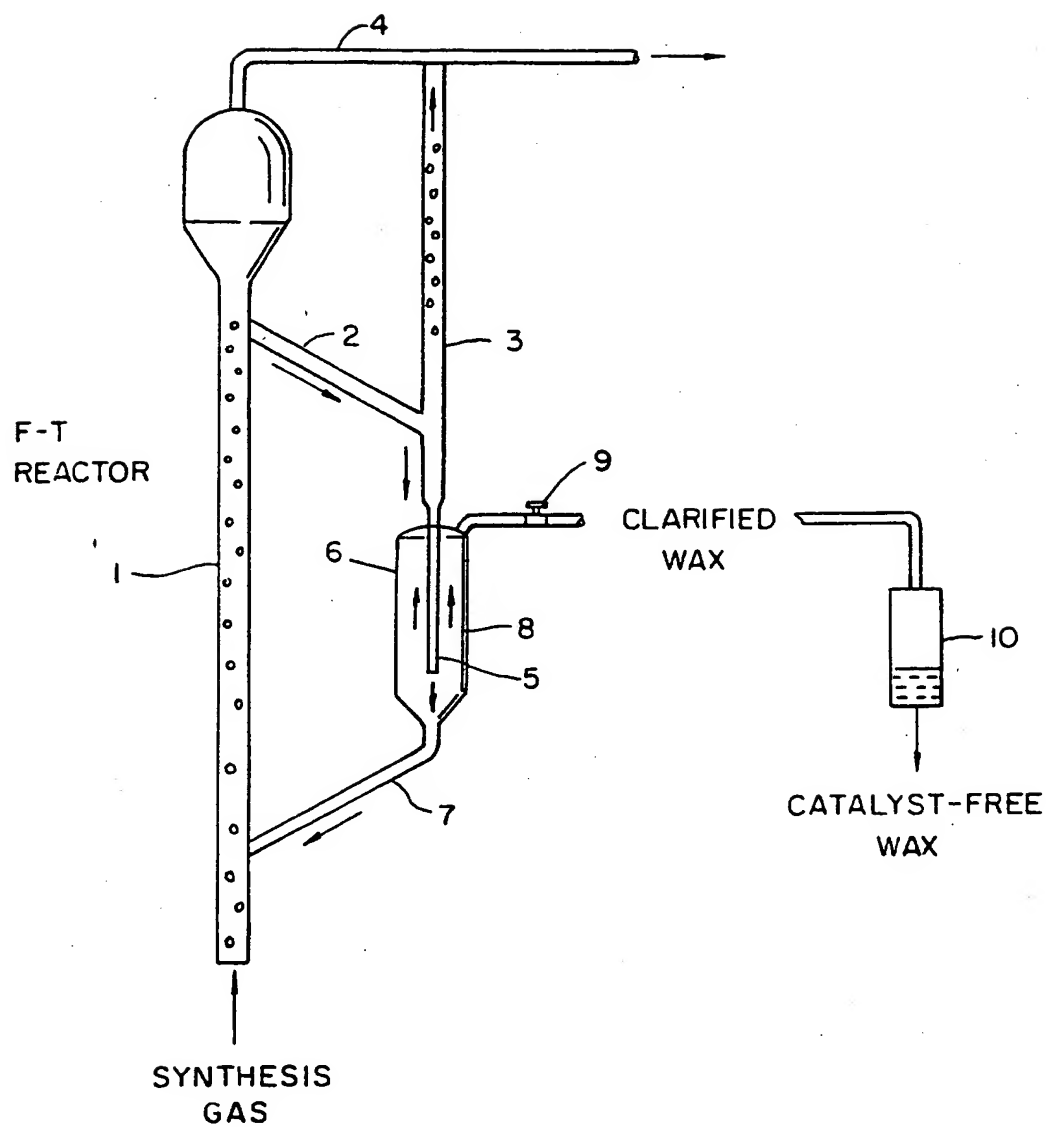


FIG. 1

CATALYST / WAX SEPARATION DEVICE

SUBSTITUTE SHEET (RULE 26)



2/4

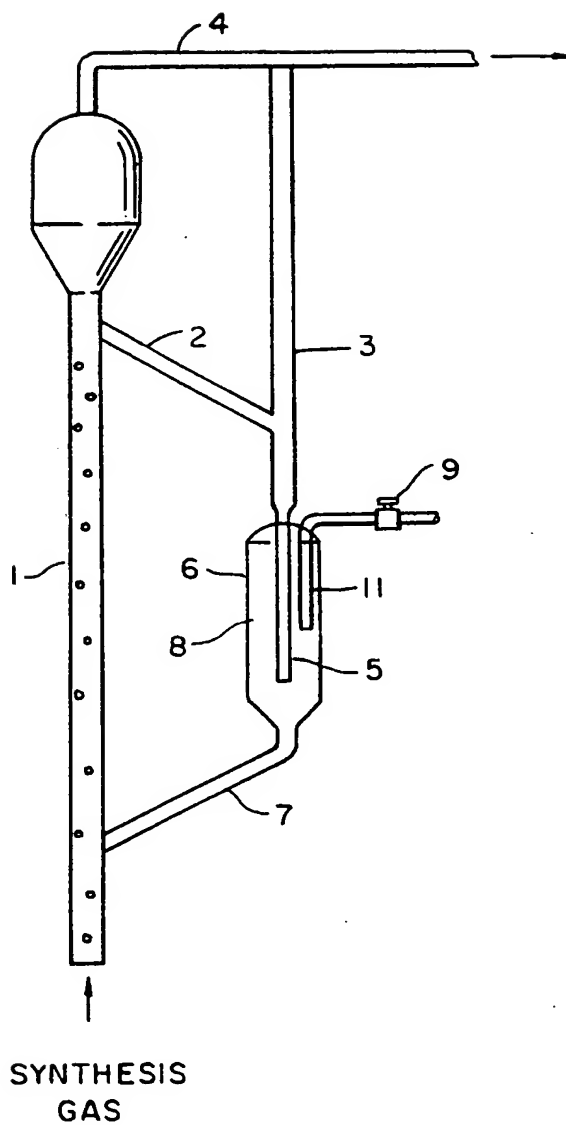


FIG. 2

3/4

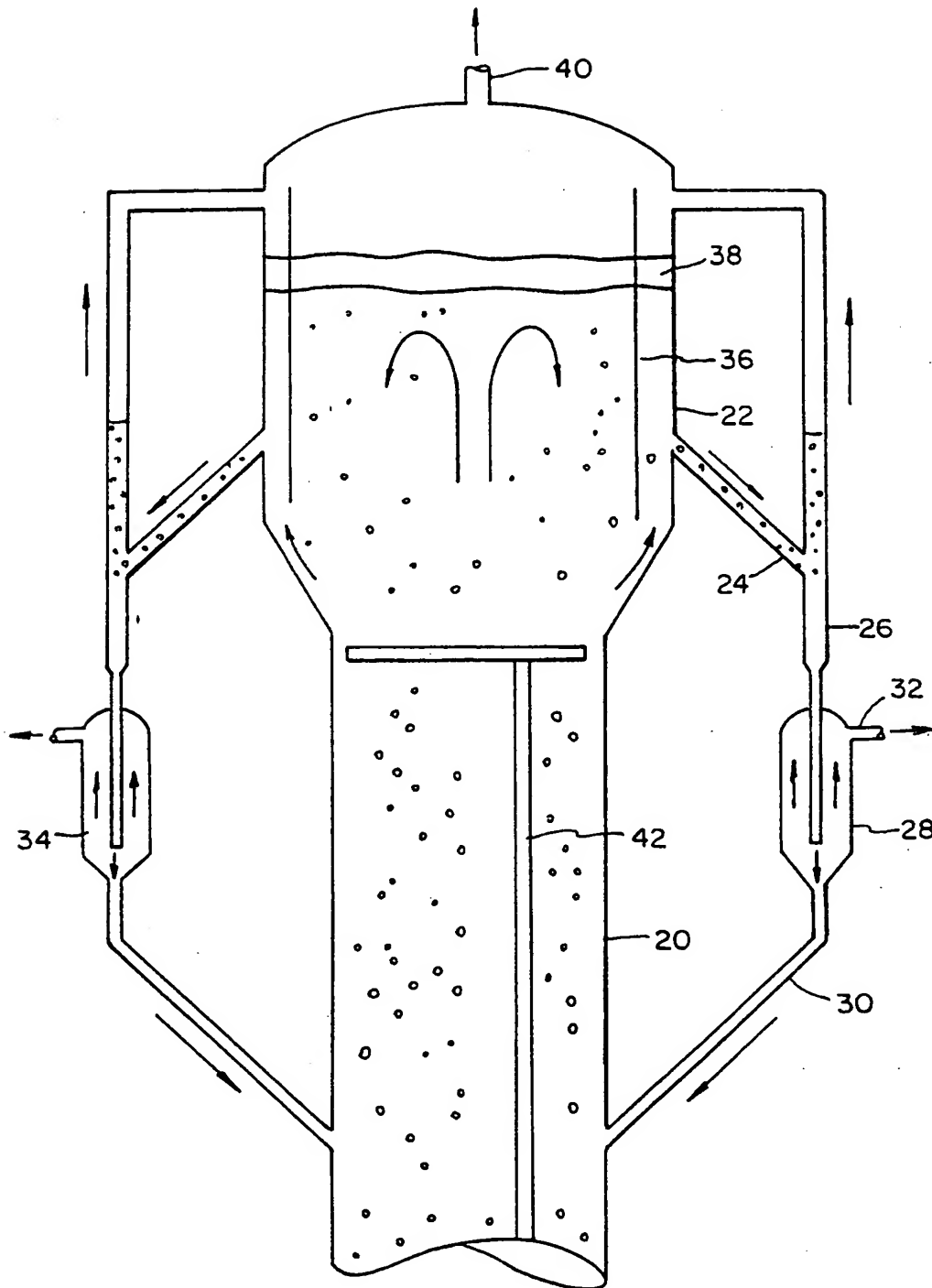


FIG. 3

SUBSTITUTE SHEET (RULE 26)

4/4

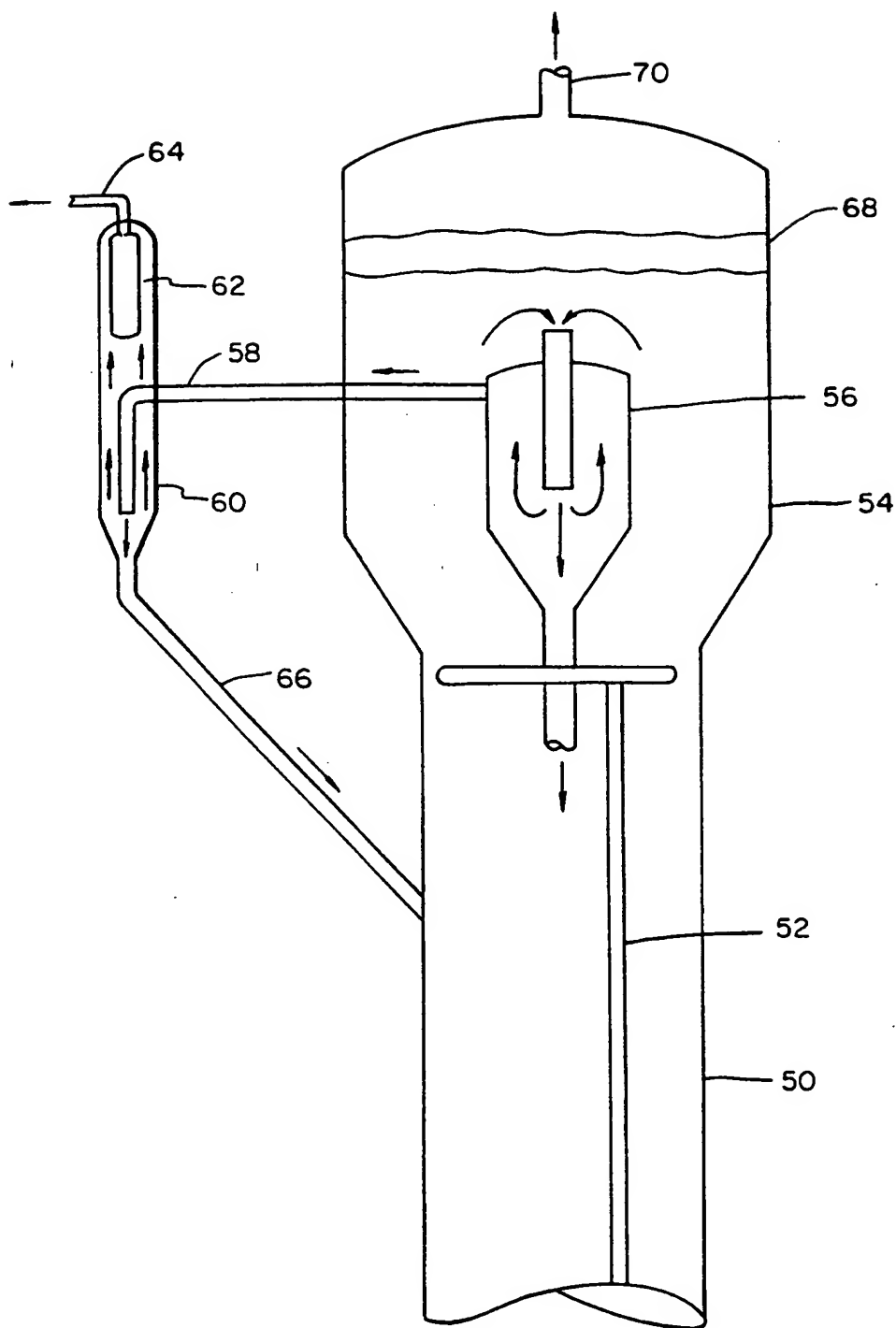


FIG. 4

SUBSTITUTE SHEET (RULE 26)

## INTERNATIONAL SEARCH REPORT

Intern: 31 Application No

PCT/US 97/23191

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C10G2/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C10G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 450 860 A (EXXON RESEARCH ENGINEERING CO) 9 October 1991 ---	
A	EP 0 609 079 A (SASOL CHEM IND PTY) 3 August 1994 ---	
A	US 5 422 375 A (RYTTER ERLING ET AL) 6 June 1995 -----	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "S" document member of the same patent family

Date of the actual completion of the international search

16 April 1998

Date of mailing of the international search report

27/04/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

De Herdt, O

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/23191

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0450860 A	09-10-1991	AU 632413 B	24-12-1992
		AU 7401591 A	10-10-1991
		CA 2038774 A	05-10-1991
		DE 69104400 D	10-11-1994
		DE 69104400 T	04-05-1995
		NO 180001 B	21-10-1996
		US 5348982 A	20-09-1994
EP 0609079 A	03-08-1994	AU 660573 B	29-06-1995
		AU 5474194 A	04-08-1994
		CA 2114275 A	28-07-1994
		JP 7000800 A	06-01-1995
		NO 940271 A	28-07-1994
		NZ 250750 A	24-02-1995
		US 5599849 A	04-02-1997
US 5422375 A	06-06-1995	ZA 9400582 A	13-09-1994
		AT 151663 T	15-05-1997
		AU 3649693 A	13-09-1993
		CN 1078486 A	17-11-1993
		DE 69309911 D	22-05-1997
		DE 69309911 T	24-07-1997
		EP 0627959 A	14-12-1994
		MX 9301054 A	31-01-1994
		NO 943122 A	24-08-1994
		WO 9316796 A	02-09-1993

**THIS PAGE BLANK (USPTO)**